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#### (54) Composition for treating cooling systems

(57) There is provided a composition for treating water cooling systems, the composition comprising a corrosion inhibitor such as polysilicate, a biocide such as stabilised chlorine dioxide and a flocculant, such as polyacrylamide.

The combination has surprising advantages and gives a general corrosion rate of less than 5 mpy with no pitting.

The use of a flocculant in the composition of the present invention enables the stripped biofilm to be completely removed and flushed from the system.

It is believed that this combination is a careful balance which overcomes the problems of scale, deposition, corrosion and microbiological fouling and would thus be effective against legionella whilst also being environmentally acceptable.

GB 2 289 672 A

**1 COMPOSITION FOR TREATING COOLING SYSTEMS**

2  
3 The present invention relates to the cleaning and  
4 sterilisation of industrial cooling towers, evaporative  
5 condensers and associated pipework/equipment. It also  
6 relates to the continuous treatment of such systems to  
7 prevent corrosion, scaling, deposition and  
8 microbiological contamination.

9  
10 Water discharged from such systems in a controlled or  
11 adventitious manner will enter factory or site drains.  
12 It is important that the materials used are of low  
13 toxicity or their discharge could adversely affect a  
14 receiving stream.

15  
16 Cooling water and its treatment still represents one of  
17 the stiffest technical challenges in industry.  
18 Arguably it is a problem which is still waiting for a  
19 final solution. There have been solutions in the past  
20 but these have been transient as further problems  
21 associated with the cooling water system have been  
22 identified or problems associated with the treatment  
23 chemicals have been discovered.

24  
25 There are four problems generally associated with  
26 cooling water systems, namely corrosion, scaling,  
27 deposition and microbiological fouling. All of these

1 problems are interrelated.

2

3 The water treatment industry has always recognised the  
4 interrelationship between these issues but has never  
5 set out to address the overall problem. The approach  
6 has always been to attack a specific problem with a  
7 specific chemical or group of chemicals and have one or  
8 two other chemicals to either assist or to mop up the  
9 consequences. At various times in the history of  
10 cooling water treatment one of the four problems shown  
11 above has assumed a greater importance and the industry  
12 has geared itself up to finding products to deal with  
13 that specific problem. In the 1960s and 1970s the  
14 problems of scale and corrosion were identified as  
15 being much more important than the other two. The lead  
16 products were therefore corrosion inhibitors and scale  
17 control chemicals and the effectiveness of a cooling  
18 water treatment was measured in terms of how good a  
19 corrosion rate and pitting index could be achieved with  
20 minimal scaling. Good corrosion inhibitors could  
21 therefore achieve corrosion rates of < 5mpy with no  
22 pitting. These products were marketed fairly  
23 aggressively by the water treatment companies with  
24 claims that their use would minimise downtime, increase  
25 thermal efficiency and give the plant operator peace of  
26 mind.

27

28 It was recognised that cooling towers were air  
29 scrubbers and that adventitious suspended solids could  
30 get into cooling water. It was also recognised that a  
31 cooling tower provides ideal conditions for  
32 microbiological growth. Dispersants and biocides were  
33 sold by the water treatment companies in support of the  
34 corrosion/scale inhibitors but these were regarded as  
35 secondary products.

36

1 Throughout the 1970s and the early 1980s scale and  
2 corrosion inhibitors were the key products in the water  
3 treatment market place and the only real change which  
4 took place was the replacement of zinc chromate  
5 formulations by more environmentally friendly products.  
6 There are few people who would argue that zinc chromate  
7 based formulations are the best cooling water  
8 inhibitors from a price and performance viewpoint that  
9 have ever been available. The factor which led to  
10 their demise is that chromium is unacceptable in a  
11 cooling water discharge to effluent. Many water  
12 treatment companies did everything they could to  
13 sustain the use of chromate based inhibitors, eg low  
14 chrome blends and effluent treatment systems.

15 There are a number of lessons to be learned from this  
16 phase of cooling water treatment.

17 1. The water treatment industry is driven by specific  
18 problems.

19 2. Many of the chemicals used in cooling water  
20 systems are relatively toxic and are eventually  
21 replaced with more environmentally friendly  
22 products.

23 3. The industry has struggled to replace the cost  
24 efficient zinc chromate formulations.

25 The 1980s saw a change in the industry's approach to  
26 cooling water treatment. Once again it was specific  
27 problem driven, and it occurred almost from the moment  
28 when cooling towers became linked with Legionnaire's  
29 Disease and water was classed as a hazardous substance.  
30 As a result the emphasis switched from scale and  
31 corrosion control to that of deposition and

1 microbiological control. Biocides and their  
2 effectiveness particularly against Legionella become  
3 the selling focus for cooling water treatments. The  
4 interest which surrounded the whole subject of  
5 Legionella control in cooling water systems caused the  
6 entire water treatment industry to re-examine its  
7 approach.

8

9 However, while the emphasis moved and marketing changed  
10 there was a dearth of innovative products. In many  
11 instances it was simply a role reversal with biocides  
12 and dispersants being promoted and scale and corrosion  
13 inhibitors being moved back to their former position of  
14 prominence. Dispersants and in particular  
15 biodispersants became necessary to allow biocides to  
16 penetrate slime deposits in cooling water systems. (In  
17 general most conventional cooling water biocides will  
18 kill bacteria with which they come into contact. They  
19 will not penetrate biofilm).

20

21 All of the codes of practice spawned by Legionnaire's  
22 Disease favoured seasonal disinfection of cooling  
23 towers/systems. This basically means that on two  
24 occasions per annum the system is thoroughly cleaned  
25 and disinfected. Most of the procedures including  
26 HS(G)70 for carrying out these seasonal disinfections  
27 focus on the use of chlorine or chlorine based  
28 materials. As it is well known that chlorine cannot  
29 penetrate biofilm the use of biodispersants is also  
30 advocated. There are a number of lessons to be learned  
31 from this phase of cooling water treatment history.

32

33 1. During this period there was a little development  
34 of biocide products but almost no development of  
35 inhibitor/scale control formulations.

36

1       2. This phase recognised the presence of biofilm in  
2       almost every water system. The water treatment  
3       industry did not give biofilms the attention which  
4       they merit and this is still very much the case.  
5       HS(G)70 and other codes of practice do not help  
6       this. They mention the existence of biofilm but  
7       fail to address it seriously.  
8

9       3. Many of the biocides which are used are fairly  
10      toxic and could not be considered as  
11      environmentally acceptable.  
12

13      It may be concluded that the water treatment industry  
14      has approached cooling water treatment by reacting to  
15      whatever problem is current rather than trying to find  
16      a more universal solution or approach. The possible  
17      solutions are becoming more restricted by environmental  
18      pressures and the range of chemicals which can be used  
19      is diminishing. Many of the previous solutions, eg  
20      chromate inhibitors, and chlorophenol and tin based  
21      biocides could not be contemplated today and some of  
22      the present solutions, eg zinc and molybdenum based  
23      inhibitors and gluteraldehyde, sulphur based and  
24      quaternary ammonium compounds are becoming unacceptable  
25      due to environmental pressure. It is not inconceivable  
26      that nitrites, phosphates and some of the milder  
27      biocides will also come under environmental scrutiny in  
28      the future.  
29

30      The presence of biofilm has been acknowledged and while  
31      some people in the industry have recognised its  
32      importance water treatment companies have largely  
33      ignored it.  
34

35      The four major problems of cleaning water cooling  
36      systems will now be discussed in detail below:

## 1        1.    CORROSION

2

3    Cooling water systems can be complex comprising an  
4    assortment of metals in a variety of configurations  
5    subjected to a wide range of different conditions  
6    (temperature, flowrate, chemical concentration). It is  
7    very probable that almost every type of corrosion  
8    mechanism will be found in a very large cooling water  
9    system (eg in a refinery or petrochemical works) during  
10   the system lifetime. The types of corrosion found in a  
11   small system may be fewer but a cross section of small  
12   systems will exhibit a full range of corrosion  
13   problems. It is surprising that water treatment  
14   companies have so few people who fully understand  
15   cooling system corrosion or who could look at a  
16   specimen and be able to give a full account of the  
17   corrosion mechanism. It is also true to state that as  
18   the large operating companies become more lean and  
19   focus on their core activities that their level of in-  
20   house expertise will reduce. Many of these companies  
21   are already almost completely reliant on their water  
22   treatment contractor and as a consequence a lot of  
23   cooling system corrosion knowledge has been lost.

24

25    There are basically two classes of corrosion, namely  
26    general wastage where the whole metal surface is  
27    affected and localised corrosion which only a small  
28    area of the metal is affected. The first class is  
29    easier to deal with; the second is more clandestine and  
30    can appear in a variety of different guises.

31

32    The prevention of corrosion in cooling water systems  
33    has been approached fairly simplistically in the past  
34    in that inhibitors which either prevent the anodic  
35    reaction or the cathodic reaction from proceeding have  
36    been used. In a new system with perfectly clean rust-

1 free surfaces where the water conditions do not change  
2 inhibition will be completely successful.  
3 Unfortunately these conditions rarely, if ever, exist  
4 and corrosion to some degree will occur in most  
5 systems. Metal surface condition is fundamental to  
6 corrosion protection and this is something which has  
7 rarely been taken into account by the bulk of the water  
8 treatment industry.

9  
10 There are numerous accounts of disastrous attempts to  
11 introduce a corrosion inhibitor into an old system  
12 which is already exhibiting a fair degree of corrosion.  
13 The water treatment industry has always relied on  
14 laboratory evaluations to determine whether a cooling  
15 water corrosion inhibitor performs well. The tests are  
16 inevitably conducted on clean specimens under ideal  
17 conditions where changes in the physical and chemical  
18 conditions of the water are carefully controlled. In  
19 almost every cooling water system there will be some  
20 factor affecting the metal surface which will affect  
21 the performance of the corrosion inhibitor. This may  
22 be millscale which has been on the metal surface prior  
23 to commissioning, surface irregularities arising from  
24 weld spatter or poor fabrication, deposition of silt on  
25 the metal surface or the formation of a biofilm on the  
26 metal. The presence of deposits, differential  
27 temperature, differential aeration, differential  
28 concentration, crevice conditions will all thwart the  
29 most efficient cooling water inhibitor. Similarly  
30 water conditions can change markedly in a cooling  
31 system because of temperature gradients, suspended  
32 matter blowing in to the sump, adventitious leaks of  
33 product and variable concentration factor.

34  
35 Cooling water inhibitors can never be fully effective  
36 and we have now appreciated that the main aim of any

1 cooling water treatment programme must be to give the  
2 inhibitor the maximum chance of performing well, ie the  
3 metal surface must be kept as clean as possible to  
4 maximise the ability of the inhibitor to reach the  
5 surface and protect the metal. If clean surfaces can  
6 be achieved a relatively inefficient inhibitor can  
7 offer better protection than a very efficient inhibitor  
8 will give in a system where surface deposits and  
9 biofouling obstruct the transport of the inhibitor to  
10 the surface of the metal.

11

12 In UK Patent No. 1,379,074 Petrey managed to prove that  
13 given deposit free surfaces a polysilicate-based  
14 inhibitor could perform as well as a zinc chromate-  
15 based formulation. In the 1960s Petrey tried to  
16 persuade the marketplace that it was possible to have a  
17 more environmentally friendly cooling water treatment  
18 but his ideas were never adopted commercially. Thirty  
19 years on, the environmental impact of cooling water  
20 treatment chemicals is a serious issue and arguably if  
21 a more environmentally acceptable treatment chemical is  
22 available it should be used.

23

24 2. SCALE

25

26 Scale in cooling water systems consists almost entirely  
27 of calcium carbonate and its presence can generally be  
28 predicted from the chemical analysis of the circulating  
29 water using Langlier and Ryznar Indices.. Once again  
30 any predictions based on these indices are general and  
31 many unexpected scaling problems have occurred in  
32 systems operating on soft water which have experienced  
33 a small alkaline process leak in a critical exchanger.  
34 The indices also do not take into account the roughness  
35 or smoothness of the metal surface or the presence of  
36 other surface foulants, all of which can be critical to

1 the initial formation and keying of the scale to the  
2 metal surface.

4 Scale poses a number of problems in cooling water  
5 systems. These are:

7 1. Loss of heat transfer. This is obvious and can be  
8 critical from a process viewpoint as in general  
9 the hotter the process the greater the tendency  
10 for scale to form on the water side leading to  
11 higher process temperatures etc. This cycle  
12 ultimately leads to condenser blockage and process  
13 shutdown on high temperature.

15 2. Resistance to flow. In the 1960s and 1970s a lot  
16 of time and attention was given to the cost of  
17 operating cooling water systems with and without  
18 surface deposits and scale. Scale effectively  
19 reduces the diameter of the pipework increasing  
20 friction losses and pumping costs. 8% to 15% of  
21 the power costs could be saved if metal surfaces  
22 were kept clean.

24 3. Poor distribution. Scale can cause blockage and  
25 partial blockages resulting in insufficient water  
26 flowing to certain parts of the system. This will  
27 tend to reduce the overall efficiency of the  
28 system as there may be preferential cooling in  
29 certain areas. Linked to this there can also be  
30 scale deposits in the cooling tower itself which  
31 can block channels leading to tower inefficiency.  
32 Ultimately scale in the tower packing can lead to  
33 packing collapse.

35 4. Treatment Absorption. One feature of scale is its  
36 ability to absorb other treatment chemicals. This

1 can increase the cost of a particular treatment  
2 and render certain biocide treatments ineffective.  
3

4 5. Scale harbours micro-environments. Scale in  
5 cooling water systems can be associated with  
6 corrosion deposits, adventitious deposits and  
7 biofilm. It can therefore be responsible for  
8 protecting certain bacteria from biocide  
9 treatment. It can also in certain situations lead  
10 to under deposit corrosion.

11

12 From the discussion so far it can be seen that it is  
13 not possible to control scaling in a cooling system by  
14 controlling the Langelier or Ryznar Index. The most  
15 cost efficient method of controlling scale is to use  
16 threshold treatment chemicals. These are chemicals  
17 which prevent the regular buildup of crystals and by  
18 deforming the crystal lattice prevent the formation of  
19 scale on a metal surface. The main advantage of  
20 threshold chemicals is that they are not dosed  
21 stoichiometrically and are therefore very cost  
22 efficient. We believe that threshold chemicals backed  
23 up with a chemical treatment which would keep the metal  
24 surface clean would provide the ultimate scale control  
25 programme. In general when a scale control programme  
26 is being used a corrosion inhibitor will not be  
27 required.

28

29 Once again we have now appreciated that control of  
30 scale depends to a large extent on controlling surface  
31 conditions and the key to successful scale and  
32 corrosion control must be to keep the surface of the  
33 metal clean.

34

35 3. DEPOSITION

36

1 The importance of keeping metal surfaces clean from  
2 corrosion products and scale has already been explained  
3 above. It is also clear that every attempt should be  
4 made to keep surfaces free from adventitious solids.

5 Suspended matter can get into the water in a cooling  
6 water system in a number of ways:

7 1. The cooling tower acts as an air-scrubber in which  
8 any solids present in the air will be transferred  
9 into the aqueous phase.

10 2. Debris left behind during the construction phase  
11 can be picked up by the water flow and perhaps  
12 transferred to a more critical part of the system.

13 3. Process leaks can produce solid material on the  
14 waterside. This would be true in situations  
15 where there is an oil or hydrocarbon leak.

16 4. Airborne material can enter the tower sump.

17 5. Algae which can form in the upper well-lit areas  
18 of some large cooling water towers can fall down  
19 under its own weight contributing suspended solids  
20 to the circulating water.

21 The composition of material found on the metal surface  
22 of any cooling system will be extremely variable. In  
23 addition to the rust/corrosion/scale deposits likely to  
24 be found there may also be a melange of silt/sand and  
25 an assortment of organic and inorganic debris. It is  
26 almost certain that there will be some microbiological  
27 activity associated with any such deposits.

28  
29  
30  
31  
32  
33  
34  
35  
36 There are a number of problems associated with

1 deposition. Severe deposition will ultimately lead to  
2 blockage or poor distribution and as it is likely to  
3 take place in low flow areas it is important that such  
4 areas do not coincide with situations where design heat  
5 transfer conditions are critical to the process.

6

7 In general most solids in the water end up in the tower  
8 sump which effectively acts as a settlement tank.

9

10 Deposits on the metal surface can promote under deposit  
11 attack by causing differential aeration conditions on  
12 the metal surface.

13

14 It is this type of attack coupled with biofouling which  
15 can create complex conditions on the metal surfaces in  
16 cooling water systems. Deposits can provide the ideal  
17 habitat for microbiological growth in that they can  
18 often provide the food as well as the cover from  
19 biocides.

20

21 Once again a situation is produced where the metal  
22 surface and the complex interactions which take place  
23 are critical to the integrity of the system from a  
24 corrosion/scaling/deposition/microbiological viewpoint.  
25 In our view if cooling water surfaces could be cleaned  
26 and maintained in a clean condition most of the  
27 problems associated with industrial water cooling  
28 systems would disappear.

29

#### 30 4. MICROBIOLOGICAL PROBLEMS

31

32 The understanding of the microbiology of a cooling  
33 water system has increased dramatically over the past  
34 twenty years. Arguably the most important discoveries  
35 have still to be made. Planktonic-free swimming  
36 bacteria rarely present any real problems to modern

1 biocide treatments and the concern today is what is  
2 happening on the various surfaces in the system. The  
3 development and maturing of biofilm on the surfaces of  
4 a cooling water system holds the key to bacterial and  
5 Legionella control in cooling systems.

6  
7 The following statements are relevant:

- 8  
9 1. Chlorine and bromine are not capable of  
10 penetrating biofilm and systems which contain a  
11 biofilm which has Legionella as part of the  
12 sessile phase and are disinfected using these  
13 biocides are capable of rapid reinfection.
- 14  
15 2. Biofilms develop rapidly on surfaces which provide  
16 a food source. This means that elastomers and  
17 plastics will promote biofilm formation before  
18 metals, particularly copper. Obviously metal with  
19 a film of organic materials will promote biofilm  
20 formation.
- 21  
22 3. Modern understanding of biofilm shows that it  
23 consists of a basal layer and a raised layer. The  
24 basal layer is only 5  $\mu\text{m}$  thick whereas the raised  
25 layer will extend into the water flow and interact  
26 with materials dissolved or suspended in the water  
27 flow.
- 28  
29 4. One of the main problems associated with the  
30 control of Legionella in water systems is  
31 associated with its growth within an adherent  
32 biofilm which comprises numerous other bacterial  
33 species, protozoa and ciliates. Together these  
34 form a complex balanced ecosystem in which the  
35 Legionella are able to express several  
36 physiological states; as planktonic cells, as free

1 living components of the biofilm ecosystem and in  
2 association with amoebae, which may become  
3 parasitised by the organism. It has been shown  
4 that the presence of iron and other nutrients will  
5 influence the type of Legionella. These factors  
6 (in particular the host, the food source, and the  
7 development of the biofilm) will all have an  
8 influence on the efficiency of any biocide  
9 treatment used to control Legionella.

10

11 It has now been appreciated that the activity at the  
12 metal surface is vital to the success of any treatment  
13 used for microbiological control in general and  
14 Legionella in particular.

15

16 New biocides capable of penetrating biofilm and killing  
17 amoeba are required.

18

19 The present invention considers all the problems faced  
20 by existing cooling water treatments in the light of  
21 some of the factors indicated in the foregoing  
22 discussion.

23

24 The criteria for a cooling water treatment programme  
25 according to the invention are:

26

27 1. The treatment must contain a constituent which  
28 will help to keep metal surfaces clean.

29

30 2. The treatment must address the problem of biofilm  
31 formation and development.

32

33 3. The materials used in the treatment must be as  
34 environmentally friendly as possible.

35

36 4. The chemicals should be easy to dose and easy to

1           test.

2

3       5. The treatments should be compatible with existing  
4       dosing systems and sterilisation techniques.

5

6       In the present invention a coagulant or polyelectrolyte  
7       is used to remove debris from cooling system surfaces  
8       by adding a biofilm penetrant and biocide, especially a  
9       stabilised chlorine dioxide formulation to the  
10      treatment package.

11

12      The philosophy behind the present invention is that if  
13      clean surfaces can be maintained a less efficient but  
14      also a much less toxic cooling water inhibitor is  
15      sufficient, for example polysilicate solutions to  
16      control corrosion when using polyelectrolytes and  
17      chlorine dioxide.

18

19      In addition a threshold chemical to prevent scaling and  
20      a maleic acid and phosphate copolymer may optionally be  
21      used.

22

23      Drinking Water Inspectorate Approvals are available for  
24      the inhibitor, biocide and polyelectrolyte/coagulants  
25      used.

26

27      The present invention provides a composition for  
28      treating water systems, said composition comprising a  
29      corrosion inhibitor, a biocide and a flocculent.

30

31      Generally, the biocide may be any chlorine dioxide  
32      based biocide. One particularly convenient biocide is  
33      stabilised chlorine dioxide, which is a buffered  
34      solution of chlorine dioxide gas in an aqueous system.  
35      Normally simple salts, such as sodium carbonate, are  
36      included to provide the buffering effect. The

1 solubility of chlorine dioxide in aqueous media is low  
2 and generally solutions higher than 5% (weight:volume)  
3 cannot normally be achieved. Any concentration of  
4 stabilised chlorine dioxide may be used in the present  
5 invention, but particular mention may be made of 2%-5%  
6 (weight:volume) concentration in the composition. The  
7 pH of the stabilised chlorine dioxide solution may be  
8 adjusted as required. For example a pH of from 7 to  
9 10, especially 7-7.5 up to 9-9.5 may be suitable.  
10 Commercially available stabilised chlorine dioxide  
11 solutions are available, such as BIOX™ from Viscona and  
12 PURAGENE™ from Vernacare. Optionally 20-30 ppm,  
13 especially approximately 25 ppm of chlorine dioxide  
14 should be generated during sterilisation procedures.

15  
16 Any chlorine dioxide may be neutralised, for example  
17 with sodium thiosulphate, prior to drainage.

18  
19 An advantage of using a chlorine dioxide based biocide  
20 is its ability to strip biofilm, the deposit of  
21 bacteria which adheres to the internal surface of pipes  
22 etc.

23  
24 Generally, the corrosion inhibitor may be a  
25 polysilicate, especially a polysilicate salt such as  
26 sodium polysilicate. Suitable quantities of  
27 polysilicate or polysilicate salt in the composition  
28 include an aqueous solution of up to 30%  
29 (weight:volume). However concentrations of less than  
30 this, for example about 8 to 15% by weight:volume may  
31 be suitable for certain systems.

32  
33 Other additives, including hydroxyethylene  
34 diphosphonate (HEDP), methylenebenzyltriazole (MBT)  
35 and/or polyacrylates (from a commercial source) may  
36 also be present, if required. Advantageously a

1      polysilicate corrosion inhibitor may be used in  
2      combination with a polyacrylate. Generally the  
3      silicate level in the treated water system will be in  
4      the region of from 20 ppm to 100 ppm, preferably 40 ppm  
5      to 60 ppm.

6

7      However, any material which acts to keep the biocide in  
8      a dispersed form may be acceptable.

9

10     The flocculant may be a polyelectrolyte (alternatively  
11    termed a "mud mover"). Such additives are known in the  
12    art and are used to flocculate solid material, thus  
13    keeping metal surfaces clean. Examples of suitable  
14    polyelectrolytes include polyacrylamides. Depending  
15    upon the system if the polyacrylamides chosen may be  
16    anionic, non-ionic or cationic. Especially suitable  
17    anionic polyacrylamides include those of low charge and  
18    with a molecular weight of 5-50kDa, especially 15-  
19    25kDa.

20

21     Suitable non-ionic polyacrylamides may be of a  
22    molecular weight of 5-50kDa, especially 15-25kDa.  
23     Suitable cationic polyacrylates include those of high  
24    charge and with a high molecular weight, for example  
25    over 50kDa.

26

27     The combination of polysilicates and polyelectrolytes  
28    has surprising advantages and gives a general corrosion  
29    rate of less than 5 mpy with no pitting.

30

31     The use of a flocculant in the composition of the  
32    present invention enables the stripped biofilm to be  
33    completely removed and flushed from the system.

34

35     The present invention further provides the use of a  
36    composition containing a corrosion inhibitor a biocide

1 and a flocculant for cleaning, and preferably  
2 sterilising, a water system.

3

4 Further, the present invention provides a method of  
5 cleaning (and disinfecting) a water system, said method  
6 comprising the addition of a corrosion inhibitor, a  
7 biocide and a flocculant to said system. It is not  
8 necessary that all the active ingredients are added  
9 together, although in certain applications that may be  
10 desirable. Thus in some situations it may be  
11 acceptable to add the ingredients sequentially.

12

13 In a further aspect, the present invention provides a  
14 kit for cleaning water systems, said kit comprising:

15

- 16 a) a corrosion inhibitor;
- 17 b) a biocide; and
- 18 c) a flocculant

19

20 wherein optionally at least one of the components  
21 listed above is packaged separately.

22

23 In a further aspect, the present invention provides the  
24 use of a corrosion inhibitor in the manufacture of a  
25 composition according to the present inhibitor.

26

27 In a further aspect, the present invention provides the  
28 use of a biocide in the manufacture of a composition  
29 according to the present inhibitor.

30

31 In a further aspect, the present invention provides the  
32 use of a flocculant in the manufacture of a composition  
33 according to the present invention.

34

35 We do not consider that the techniques and chemicals  
36 which are used at present and are advocated by the

1     Health and Safety Executive can guarantee the  
2     elimination of Legionella risk from cooling water  
3     systems. Work has indicated that the biocides  
4     currently used, and particularly the halogens, will not  
5     penetrate biofilm or destroy the amoeba which can act  
6     as host for the Legionella bacterium. CAMR have for  
7     instance reported that a bromine level of 8 mg/l had no  
8     effect on Legionella hidden in a surface biofilm and  
9     work at Sheffield (Hallam) University has indicated the  
10    failure of chlorine to kill host Amoeba when used at  
11    levels recommended by HS(G)70.

12

13    It is also the experience of the water treatment  
14    companies and cooling tower operators that following  
15    the recommendations of HS(G)70 does not necessarily  
16    prevent proliferation of Legionella bacteria. The  
17    complexity of cooling water systems, the variety of  
18    different materials and the possibility of amoeba and  
19    biofilm hideout means that current thoughts on  
20    acceptable biocides may not be valid.

21

22    We believe that chlorine dioxide is a fundamental  
23    ingredient of any water treatment which claims to be  
24    effective against Legionella. There is already a body  
25    of practical information available to suggest that  
26    chlorine dioxide can penetrate and remove biofilm. On  
27    many occasions large quantities of biofilm have been  
28    removed from systems which had been recently  
29    disinfected with chlorine. This will be the claim of  
30    many operators who routinely use chlorine dioxide for  
31    sterilisations or for those who have been asked to  
32    perform a sterilisation on a cooling tower which has  
33    been routinely disinfected using hypochlorite solution  
34    and is disinfected for the first time using chlorine  
35    dioxide. It is one of the underlying claims of the  
36    Liverpool Broadgreen Hospital report where chlorine

1 dioxide replaced bleach as the biocide and removed the  
2 Legionella risk from the hospital hot water systems  
3 which had been the cause of recurring Legionella  
4 problems while operating on a chlorine based regime.

5

6 Chlorine dioxide has found little application as a  
7 cooling water treatment biocide in the past and there  
8 have been good reasons for this.

9

10 1. Almost all of the chlorine dioxide used for water  
11 treatment was produced using generators.

12 Generators got themselves a bad reputation in the  
13 past as some of the early ones were poorly made  
14 and managed to blow themselves apart. Chlorine  
15 dioxide generators represent a fair capital  
16 investment which would not be considered  
17 appropriate for many small and medium sized  
18 cooling water systems.

19

20 2. Chlorine dioxide cannot be transported and must be  
21 produced on site. This involves the handling of  
22 chemicals which would be considered as hazardous.

23

24 3. While much is known about chlorine dioxide as a  
25 disinfectant in the potable water treatment  
26 industry little is known about it as a cooling  
27 water biocide. There are in fact few bacterial  
28 and viral strains against which chlorine dioxide  
29 is not completely effective.

30

31 4. The advent of stabilised chlorine dioxide to this  
32 country is relatively recent and all the major  
33 water treatment companies have decided not to add  
34 it to their product portfolio at present. This is  
35 a decision which they will almost certainly revoke  
36 as information on the effectiveness of these

1 products becomes more widespread.

2

3 5. Stabilised chlorine dioxide has been compared

4 unfairly with bleach (14.5% free chlorine) as a

5 disinfectant in situations where it is used as a

6 direct replacement. If it is assumed that bleach

7 can be sold for around £0.35/litre and chlorine

8 dioxide is 7 times more efficient than chlorine

9 then a 2% chlorine dioxide solution should be

10 roughly the same price, ie £0.35/litre. In fact

11 the price will be roughly 10 times this and one of

12 the greatest hurdles which stabilised chlorine

13 dioxide will have to leap is this invidious price

14 comparison with bleach. The material cost

15 competes well with the other commonly used

16 biocides.

17

18 It is clear from the more recent outbreaks of

19 Legionnaire's Disease that a new product needs to be

20 used as the standard disinfectant in water systems, and

21 in particular the more complex cooling water systems.

22 We believe that this need is fulfilled by the

23 composition of the present invention.

24

25 The value of a thorough clean and disinfection using

26 chlorine dioxide should not be understated. If a

27 system can be brought to a condition of "industrial

28 sterility" then ongoing treatment becomes

29 straightforward and relatively non problematic.

30

31 People require to change their thinking about the

32 importance of the seasonal disinfection. It is not

33 something that is done twice per annum as a

34 microbiological purging of the system. It is something

35 that is done to give the Delta PA treatment a firm

36 foundation. Often after this first disinfection

1 microbiological control can be effected by dosing the  
2 stabilised chlorine dioxide based product without  
3 activation.

4

5 When the biofilm has been completely removed and it is  
6 only adventitious bacteria entering the system which  
7 need to be dealt with then the stabilised material can  
8 activate itself on the acidic cell wall of the  
9 bacterium releasing the chlorine dioxide will kill the  
10 bug.

11

12 This sort of situation required careful monitoring and  
13 any sudden increases in microbiological population  
14 needs to be addressed by activating the product. The  
15 level of activation will depend on the type of system  
16 and the particular problem.

17

18 Some systems only need a shock dose perhaps once or  
19 twice per week to control the bug count; others may  
20 require a variation between of stabilised and activated  
21 chlorine dioxide.

22

23 A further constraint on dosing is that the DELTA PA  
24 Programme is being marketed as being environmental  
25 friendly and the ongoing treatment level should if  
26 possible be confined to 1 mg/l to 3 mg/l.

27

28 It is for this reason that the effectiveness of the  
29 disinfection is stressed. When it is conducted  
30 properly and the neutralisation of residual chlorine  
31 dioxide has been completed then the system should be  
32 controlled by low level dosing of the DELTA PA 6 range.  
33 Any sudden increase in the chlorine dioxide demand must  
34 be treated as an emergency situation requiring a mini  
35 on-line disinfection with neutralisation of any  
36 blowdown from the system.

1       **EXAMPLE**

2       3       While each cooling water system treatment regime is  
3       4       customised the treatment proposed uses three chemicals:

5       6       1.    DELTA PA 4    Series which are inhibitors based  
6       7       on sodium polysilicate

8       9       2.    DELTA PA 6    Series of biocides which are based  
10      10      on "BIOX" a stabilised chlorine  
11      11      dioxide product.

12      13      3.    DELTA PA 8    Series of flocculant materials.

14      15      The inhibitor and the flocculant are dosed in  
16      16      proportion to the make up water to the system. The  
17      17      concentration in the make up will depend on the  
18      18      concentration factor in the system but we would  
19      19      normally expect a silicate level of 20ppm to 30ppm.  
20      20      The flocculant is dosed at a level of 10ppm to 100ppm  
21      21      depending on the product used.

22      23      The biocide can be dosed in a variety of ways eg  
24      24      continuously, on a batch basis, or depending on  
25      25      circumstances both. The biocide be dosed in the  
26      26      activated or non-activated form but generally at a  
27      27      maximum level of 1 or 2ppm in the cooling water. At  
28      28      the use level none of the materials used can have an  
29      29      adverse effect on the stream which receives the  
30      30      blowdown water from the cooling water system.

31      32      Experimental work has shown:

33      34      1.    The DELTA PA system achieves corrosion rates of <3  
35      35      mpy and no pitting on mild steel. Corrosion rates  
36      36      on copper, copper alloys and stainless steel are

1           <1 mpy.

2

3       2. Metal surfaces are kept free from biofilm and  
4           surface debris. This improved heat transfer and  
5           therefore energy efficiency improves the overall  
6           performance of the cooling water system.

7

8       3. All of the chemicals used are used in the  
9           treatment of potable water, are all approved by  
10           the Drinking Water Inspectorate and therefore are  
11           of low toxicity. This has been confirmed by  
12           Microtox testing.

13

14       4. The treatment is more effective if started  
15           immediately after a clean and sterilisation of the  
16           cooling tower using chlorine dioxide and polymer.  
17           The DELTA PA 6 product is activated and dosed at a  
18           rate to give 20 ppm ClO<sub>2</sub> in the cooling water.

19

20           The DELTA PA 8 product is dosed to ensure that  
21           biofilm and debris removed by the clean are  
22           dispersed and flocculated suitable for removal  
23           from the system. The unused chlorine dioxide in  
24           the waste water from the clean is treated with  
25           sodium thiosulphate or hydrogen peroxide prior to  
26           discharge.

27

28       5. The DELTA PA system lends itself to chemical  
29           cleaning of critical heat exchangers fouled with  
30           biofilm and iron oxide by adding inhibited citric  
31           acid with the DELTA PA 6 and DELTA PA 8 product.  
32           These cleans can be conducted on or off line  
33           depending on circumstances.

34

35           The chemicals which comprise the range to date are  
36           therefore:

1 DELTA PA 400 Series inhibitors and scale control  
2 chemicals.

4 DELTA PA 441 polysilicate concentrate 29% SiO<sub>2</sub> dosed to  
5 give 10 to 30 ppm product in the system. This product  
6 is used for large systems.

8      DELTA PA 442 is a 1:1 dilution of this product and  
9      DELTA PA4410 is a 10:1 dilution of this product.

10  
11 DELTA PA 450 polysilicate and multichemical formulation  
12 dosed to give 70 ppm to 100 ppm in the system. This  
13 chemical is used in multimetal systems where something  
14 more efficient than a basic polysilicate is preferred.  
15 It is less environmentally friendly than DELTA PA 441.  
16 This formulation is also available as a 5:1 dilution  
17 called DELTA PA 445.

19 DELTA PA 470 polymer and phosphonate for threshold  
20 effect scale inhibition. This is dosed at 25 ppm to 40  
21 ppm. Available as DELTA PA 471 which is a 1:1 dilution  
22 of DELTA PA 4710 as a 10:1 dilution.

## 24 DELTA PA 6 Series biocides.

26 The biocides are based on stabilised chlorine dioxide  
27 and comprise DELTA PA 62 a (2% stabilised chlorine  
28 dioxide solution) and DELTA PA 65 (a 5% stabilised  
29 chlorine dioxide solution).

31 The formulations may contain biodegradable surfactants  
32 and are less highly buffered than the conventional  
33 products. The real value of these products is in the  
34 range of activation techniques which could be used.

### 3.6 DELTA PA 8 Series: Coagulants and polymers.

1 A full range of cationic organic coagulants based on  
2 organic materials (non aluminium) are included in the  
3 programme..

4

5 A full range of polyelectrolytes is included in the  
6 range although there is a core of three products  
7 representing cationic, non ionic and anionic products.

8

9 Anionic polymers are best suited to inorganic and inert  
10 debris, eg silt and sand, while a strong cationic  
11 polyelectrolyte is best suited to oily deposits and  
12 organic debris.

13

14 We believe that the incorporation of chlorine dioxide  
15 into the microbiological control package is fundamental  
16 to Legionella control because the PA 6 series of  
17 biocides offers something that other commonly used  
18 biocides do not.

19

1      CLAIMS

2      1. A composition for treating water systems, said  
3      composition comprising a corrosion inhibitor, a  
4      biocide and a flocculant.

5

6      2. A composition as claimed in Claim 1 wherein said  
7      biocide is based on chlorine dioxide.

8

9      3. A composition as claimed in Claim 2 wherein said  
10     biocide is a buffered solution of chlorine dioxide  
11     gas in an aqueous system.

12

13     4. A composition as claimed in either one of Claims 2  
14     and 3 wherein the concentration of chlorine  
15     dioxide is 2% to 5% (weight : volume).

16

17     5. A composition as claimed in any one of Claims 1 to  
18     4 wherein said corrosion inhibitor is a  
19     polysilicate.

20

21     6. A composition as claimed in Claim 5 where the  
22     concentration of polysilicate is up to 30% (weight  
23     : volume).

24

25     7. A composition as claimed in any one of Claims 1 to  
26     6 wherein said flocculant is a polyacrylamide.

27

28     8. A composition as claimed in any one of Claims 1 to  
29     7 which further comprises hydroxydiphosphonate  
30     (HEDP), methylenebenzyltriazole (MBT) and/or  
31     polyacrylates.

32

33     9. Use of a composition as claimed in any one of  
34     Claims 1 to 8 for cleaning a water system.

35

36

1 10. A method of cleaning a water system, said method  
2 comprising the addition of a corrosion inhibitor,  
3 a biocide and a flocculant to said system.  
4

5 11. A kit for cleaning water systems, said kit  
6 comprising:  
7

8 a) a corrosion inhibitor;  
9 b) a biocide; and  
10 c) a flocculant  
11  
12 wherein optionally at least one of the components  
13 listed above is packaged separately.  
14

15 12. A composition for treating water systems  
16 substantially as defined in the Example.



Application No: GB 9510498.0  
Claims searched: 1-12

Examiner: Diane Davies  
Date of search: 9 August 1995

**Patents Act 1977**  
**Search Report under Section 17**

**Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.N): C1C

Int Cl (Ed.6): C02F

Other: Online databases: EDOC, JAPIO, WPI

**Documents considered to be relevant:**

Category	Identity of document and relevant passage	Relevant to claims
X	GB 2126579 A (Buckman Labs Inc.) Ammonium salts which act as flocculants, mircobiocides and corrosion inhibitors.	1
X	US 4790943 A (SE Water Conservation Systems Inc) Treatment of waste water with biocide and flocculants	1-12
X	DE 2520360 A (Wabag Wasserreinig) Use of oxidant and flocculant to purify and sterilise water from swimming pools.	1-12
X	GB 1381673 A (J. O'Shea <i>et al</i> ) A method of chemical treatment of water supplies, see in particular the list of chemicals on page 3.	1-12

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.